

## APPLICATION OF NEW PARTITION COEFFICIENTS TO MODELING PLAGIOCLASE.

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**Introduction:** Previously, studies that determined the partition coefficient for an element,  $i$ , between plagioclase and the residual basaltic melt ( $D_i^{\text{plag}}$ ) have been conducted using experimental conditions dissimilar from the Moon, and thus these values are not ideal for modeling plagioclase fractionation in a lunar system. However, recent work [1] has determined partition coefficients for plagioclase at lunar oxygen fugacities, and resulted in plagioclase with Anorthite contents  $\geq \text{An}_{90}$ ; these are significantly more calcic than plagioclase in previous studies, and the An content has a profound effect on partition coefficient values [2,3].

Plagioclase D-values, which are dependent on the An content of the crystal [e.g., 2-6], can be determined using published experimental data and the correlative An contents. Here, we examine new experimental data from [1] to ascertain their effect on the calculation of equilibrium liquids from Apollo 16 sample 60635,2. This sample is a coarse grained, subophitic impact melt composed of ~55% plagioclase laths with  $\text{An}_{94.4-98.7}$  [7,8], distinctly more calcic than of previous partition coefficient studies (e.g., [3-6, 9-10]).

Sample 60635,2 is notable as having several plagioclase trace element analyses containing a negative Europium anomaly (-Eu) in the rare-earth element (REE) profile, rather than the typical positive Eu anomaly (+Eu) [7-8] (Fig. 1). The expected +Eu is due to the similarity in size and charge with  $\text{Ca}^{2+}$ , thereby allowing  $\text{Eu}^{2+}$  to be easily taken up by the plagioclase crystal structure, in contrast to the remaining  $\text{REE}^{3+}$ . Some 60635,2 plagioclase crystals only have +Eu REE profiles, some only have -Eu REE profiles, and some +Eu and -Eu analyses in different areas on a single crystal [7, 8]. Moreover, there does not seem to be any core-rim association with the +Eu or -Eu analyses, nor does there appear to be a correlation between the size, shape, or location of a particular crystal within the sample and the sign of its Eu anomaly, which suggests a complex evolution.

In order to investigate this sample further, we can calculate the equilibrium liquids, but with An contents distinct from previous experimental studies, we must calculate the appropriate partition coefficients for each trace element analysis.

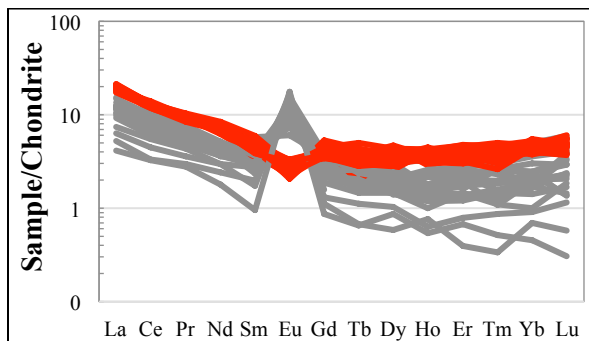


Fig. 1. REE profiles of 60635,2 plagioclase with +Eu (grey lines) and -Eu (red lines) anomalies.

**Modified Bindeman Method:** We employ a modified method of determining partition coefficients by An content based on the work of [2,3], which we refer to as the 'modified Bindeman method.' We have incorporated the new experimental data from [1] with data published by [2; 9-11] to calculate updated regression lines for correlating D-values with An content of analyses from 60635,2

Anorthite contents of 60635 plagioclase were quantified using the JEOL JXA-8200 electron microprobe at Washington Univ. in St. Louis (see [7,8] for instrument setup and calibration); trace element contents were determined using the Thermo Finnigan Element2 inductively coupled plasma-mass spectrometer coupled with a New Wave 213 nm laser ablation system at the Midwest Isotope and Trace Element Research Center at the Univ. of Notre Dame (see [7,8] for instrument setup and calibration).

**Regressions and D calculations:** The addition of the new data from [1] has resulted in improved regressions for several elements when using the modified Bindeman method (Table 1), including some for which regressions were previously irrelevant due to a low correlation coefficient (R). We find that an improved R-value can be seen for several elements following the inclusion of data from [1] (Table 1). Most importantly, the new data now allow for a regression for Gd and Ho, as well as for Tb and Dy; previously, the regressions for these elements resulted in  $R < 0.1$ , which did not allow for the calculation of reliable D-values based on An content. In contrast, the correlation coefficient for some elements have

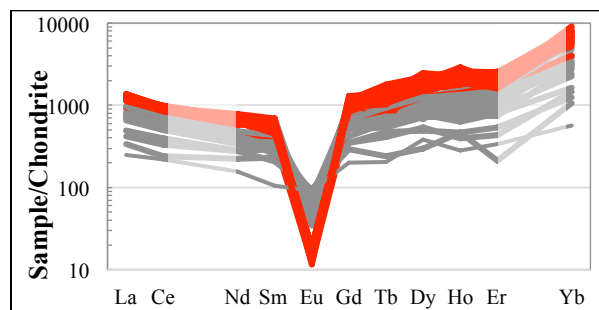
decreased with the addition of the new D-values, but is still  $R > 0.7$  (e.g., Yb, Table 1).

Element	Without data from [1]	With data from [1]
Sr	0.857	0.831
Y	0.599	0.718
La	0.782	0.814
Ce	0.719	0.791
Nd	0.726	0.777
Sm	0.641	0.711
Eu	0.025	0.826*
Gd	0.021	0.706
Tb	0.055	0.593
Dy	0.001	0.643
Ho	0.002	0.776
Er	0.715	0.705
Yb	0.906	0.798

**Table 1.** Correlation Coefficient (R-value) of D-value regressions made without data from [1] and with data from [1]. \* indicates regression only using values below I-W  $fO_2$ .

A regression line for Eu was previously calculated using data from [4,9-11], but the enormous scatter from the various experimental conditions resulted in a meager R-value, even when including the new data from [1] because Eu is particularly sensitive to the  $fO_2$  (e.g., [10]). If, however, a regression is made using only data from experiments at or below I-W  $fO_2$  conditions, which is more representative of the lunar environment (e.g., [12]), then the regression dramatically improves (Table 1).

**60635,2 -Eu anomaly Plagioclase:** With the improved regressions, we are now able to reliably calculate the appropriate D-values and therefore equilibrium liquid compositions of the plagioclase crystals using most of the REE, including Eu (Fig. 2). These show that the +Eu and -Eu plagioclase analyses originated from liquids depleted in Eu (0.65 to 5.31 ppm) and enriched in the heavy REE (Fig. 2).

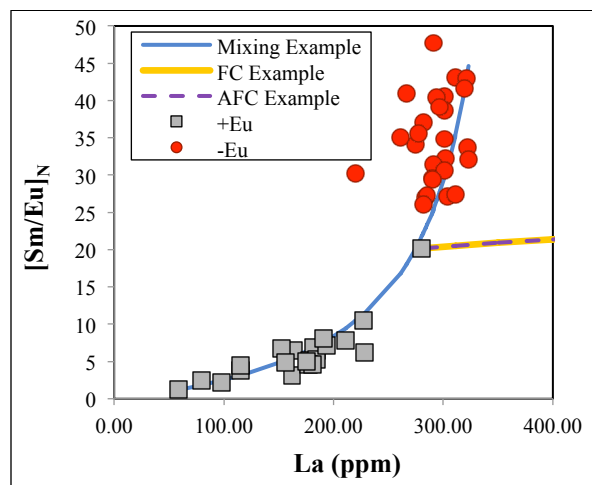


**Fig. 2.** Equilibrium Liquid (EL) REE profiles of 60635,2 plagioclase. EL from plagioclase analyses with +Eu are grey, whereas EL from analyses with -Eu are red. At this time, regressions are not possible for Pr, Tm, and Lu due to inadequate experimental data, hence these are not included in the figure above. Light grey and light red lines indicate where data is extrapolated.

We have modeled fractional crystallization (FC) and FC with assimilation (AFC) using contaminants

that are also depleted in Eu, but enriched in the other REE, such as QMG and Whitlockite-rich QMG (formerly QMD and W-QMD, respectively [e.g., 13]), as well as various KREEP compositions (e.g. [14,15]). However, despite some models eventually crystallizing plagioclase with -Eu anomalies, all of the REE are too enriched at that point, and the chondrite-normalized Sm/Eu ratio ( $[Sm/Eu]_N$ ) does not match well with the calculated liquids (Fig. 3). Therefore, we present a simple mixing model using two of the liquid compositions as the end-members, which results in a better fit of the data (Fig. 3).

**Implications:** Preliminary models suggest that the anomalous plagioclase data from 60635,2 can be accounted for via a simple mixing model of two impact melt compositions. Mixing model attempts using other materials suggested above (e.g., KREEP) do not match the liquids, although the search for an appropriate end-member composition is ongoing and further calculations will be conducted to determine other suitable end-member compositions (such as via [16]).



**Fig. 3.** Calculated equilibrium liquids with examples of a two-component mixing model, FC model, and AFC model.

**References:** [1] Rapp J.F. et al. (submitted), *GCA*. [2] Bindeman I.N. et al. (1998) *GCA* 62, 1175-1193. [3] Blundy J.D. & Wood B.J. (1991) *GCA* 55, 193-209. [4] Hui H. et al. (2011) *GCA* 75, 6439-6460. [5] Bédard J.H. (2006) *GCA* 70, 3717-3742. [6] Tepley F.J., III et al. (2010) *Lithos*, 118, 82-94. [7] Fagan A.L. & Neal C.R. (2012) *Lunar Planet. Sci. Conf. XLIII*, #1426. [8] Fagan A.L. (2012) PhD Dissertation, Univ. Notre. [9] Bindeman I.N. & Davis A.M. (2000) *GCA* 64, 2863-2878. [10] Aigner-Torres M. et al. (2007) *Contrib. Mineral. Petrol.* 153, 647-667. [11] Blundy J. (1997) *Chem. Geol.* 141, 73-92. [12] Sato M. et al. (1973) *Proc. Lunar Sci.* 4, 1061-1079. [13] Jolliff B.L. (1991) *Proc. Lunar Sci.* 21, 101-118. [14] Lindstrom M.M. et al. (1988) *Proc. Lunar Sci.* 18, 169-185. [15] Warren P.H. (1989) *Wkshp. Moon in Transition*, 149-153. [16] Powell R. (1984) *J. Geol. Soc. London*, 141, 447-452.